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Description

1. Field of the Invention

This invention relates to catalysts made either of porous titania or of a mixture of porous titania with another porous inorganic oxide, which contain additional ingredients such as oxides of vanadium and tungsten for the reduction of nitrogen oxides by ammonia.

2. Description of the Previously Published Art

Nitrogen oxides have been selectively reduced in the presence of ammonia and various types of catalysts.

U. S. Patent No. 4,048,112 discloses a catalyst for the selective reduction of nitrogen oxides in exhaust gases in the presence of ammonia. The catalyst is made of vanadium oxide supported on a carrier of titanium oxide in the anatase form.

U. S. Patent No. 4,085,193 discloses catalysts for removing NO_x . Among the materials disclosed is titania and at least an oxide of molybdenum, tungsten, iron, vanadium, nickel, cobalt, copper, chromium or uranium.

U. S. Patent No. 4,010,238 discloses a process to remove NO_x in the presence of ammonia and a vanadium oxide catalyst of the formula $\text{V}_x\text{A}_y\text{O}_z$ where V is vanadium, A is Cu, Zn, Sn, Pb, Ti, P, Cr, Fe Co and Ni, x and y are each a numeral of 0.5 to 12 and z is a numeral of 1 to 60.

U. S. Patent No. 4,225,462 discloses using barium sulfate and vanadium (IV) oxide sulfate to make a water resistant catalyst for reducing nitrogen oxide with ammonia.

U. S. Patent No. 4,176,089 discloses making high surface area, low bulk density mixed silica-titania materials useful for catalysts for the selective reduction of nitrogen oxides with ammonia. The catalysts are made by premixing the alkoxides of titanium and silicon and adding the premixed alkoxides to a hydrolysis medium so as to form a silica-titania precipitate.

U. S. Patent No. 4,188,365 discloses a catalyst for the vapor phase reduction of nitrogen oxides with ammonia. The catalyst has a catalytic metal compound on a shaped carrier of TiO_2 and a clay mineral having an average particle size of 0.1 to 100 microns. The shaped carrier can also contain inorganic fibrous material and small particles of silica hydrogel and silica sol.

U. S. Patent No. 4,221,768 discloses a process to remove nitrogen oxides with ammonia by using a catalyst made of an intimately mixed binary ($\text{TiO}_2\text{-SiO}_2$) or ternary ($\text{TiO}_2\text{-ZrO}_2\text{-SiO}_2$) oxide with no cladding and with no co-precipitation. These binary and ternary oxides are not mere mixtures of the individual oxides.

Great Britain Patent No. 2,149,680 discloses a catalyst for the removal of nitrogen oxides made of (A) 80 to 95% by weight of an oxide obtained by thermal treatment of either binary hydrous oxide of titanium and silicon, a binary hydrous oxide of titanium and zirconium or a ternary hydrous oxide of titanium, zirconium and silicon in the presence of sulfuric acid or ammonium sulfate, (B) from 0 to 5% by weight of vanadium oxide, and (C) from 1 to 15% by weight of an oxide of tungsten, molybdenum, tin or cerium.

U. S. Patent No. 4,280,926 (and its divisional 4,520,124) form a slurry of 1-20 mm long fibers which can be a silica fiber with diameter of 0.1-30 microns. Then either TiO_2 or Al_2O_3 forming materials are added and a sheet is made by papermaking means. These sheets can be formed into a honeycomb structure. The sheets are then impregnated with catalytically active agents.

U. S. Patent No. 4,113,660 discloses making a titania catalyst using a metatitanic acid sol or gel.

T. Shikada et al. in "Reduction of Nitric Oxide by Ammonia over Silica Supported Vanadium Oxide Catalysts (III). Effects of Additives" in *Nenryo Hyokai Shi*, vol. 58 page 1055 (1979) disclose treating silica gel with titanic sulfate solution, neutralizing with ammonia water, drying, adding vanadyl oxalate solution, drying and finally calcining in air at 350 °C for 3 hours to produce a catalyst for the reduction of nitric oxides by ammonia. They found that the amount of TiO_2 required for modifying the surface of the silica is not high. A 3% level was sufficient and that as the TiO_2 content increased beyond this point the activity declined.

U. S. Patent No. 4,705,770 discloses making an attrition resistant catalyst from titanyl sulfate which can be used in a fluidized bed. Small particles are made for fluidization. There appears to be no discussion of macroporosity; all the mean pore diameters are 232 Angstrom units or less. Furthermore, they do not intend to form a shaped support which has macroporosity.

EP-A-0 268 265 discloses a denitration catalyst comprising an oxide of titanium, an oxide of tungsten and an oxide of vanadium as catalytically active ingredients and having a pore volume of 0.1 to 0.5 cm^3/g .

The titania content is 50 to 99 wt% and the catalyst may further contain silica.

3. Objects of the Invention

It is an object of this invention to enhance the catalyst NO_x removal performance and reduce the manufacturing cost of an SCR catalyst.

It is a further object of this invention to extend the catalyst life by improving the poison resistance.

It is a further object of this invention to reduce the manufacturing cost by reducing the amount of titania employed in the monolith structure of an SCR catalyst.

It is a further object of this invention to reduce or limit the SO₂ oxidation activity while at the same time enhancing NO_x removal activity.

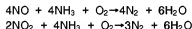
It is a further object of this invention to reduce the operating temperatures for given NO_x removal requirements.

It is a further object of this invention to reduce the required reactor volume for a given NO_x conversion and hence simultaneously reduce the reactor pressure drop.

It is a further object of this invention to reduce the unreacted ammonia at the exit of the SCR reactor.

These and further objects will become apparent as the description of the invention proceeds.

The feasibility of NO_x removal through selective catalytic reduction with NH₃ in the presence of O₂ has been known for sometime and proceeds as follows:



In contrast to previous NO_x removal (DeNO_x) catalysts which utilize a bulk titania support, we have obtained a superior catalyst consisting of titania particles with the appropriate catalytic metal oxide function with the proper porosity either alone or mixed with particles of a porous inorganic oxide. Based on reaction engineering principles, we have successfully mathematically modeled the overall catalytic DeNO_x reaction under various conditions. Further mathematical catalyst optimization studies have led us to uncover a route to improved DeNO_x catalysts. Our model predicts that catalysts having a fraction of pores larger than 60 nm (600 Angstrom units) will have better activities than those without these large pores. As will be described below, we have successfully obtained catalysts incorporating this porosity and, as predicted by our mathematical modeling, the DeNO_x activity is superior to that of commercially available catalysts which contain very few or no pores larger than 60 nm (600 Angstrom units). Furthermore, by partially replacing the expensive bulk titania by a low-cost porous metal oxide, the cost of preparing the catalyst is substantially reduced while the strength of the catalyst is increased.

In one embodiment the catalyst is made of titania particles alone where the formed catalyst has the proper porosity in pores larger than 60 nm (600 Angstrom units). An optional feature of this embodiment is that porous inorganic oxide particles can be mixed in an amount up to 40% by weight to produce a formed support which has a total porosity of up to 0.80 cm³/cm³ of the formed catalyst which is made up of a micropore porosity (comprising pores having a pore diameter 60 nm (600 Angstrom units) or less) of 0.05 to 0.5 cm³/cm³ and a macroporosity (comprising pores having diameters greater than 60 nm (600 Angstrom units)) of 0.05 to 0.5 cm³/cm³. The titania is present substantially in the anatase phase. The catalyst is made by depositing on the support a metal oxide catalytic component such as V₂O₅, MoO₃, WO₃, Fe₂O₃, CuSO₄, VOSO₄, SnO₂, Mn₂O₃, Mn₂O₄, or mixtures thereof. Preferably the metal oxide is present in an amount from a catalytically effective amount to 25% by weight of the entire catalyst.

According to said optional feature the titania particles can be mixed with particles of a porous inorganic oxide such as SiO₂, Al₂O₃, ZrO₂, AlPO₄, Fe₂O₃ and B₂O₃ and mixtures thereof. The particles of titania or said mixture may be formed, for example by extrusion, into a useful catalyst support shape such as a monolith, extrudate, bead or plate.

In another embodiment of the invention, barium sulfate is added to the surface of the inorganic oxide such as SiO₂ to make an improved support. This can either be done by the direct addition of barium sulfate or by adding a barium compound which will form barium sulfate in situ. The TiO₂ can be added either concurrently with or following the addition of the barium sulfate. When a catalytic metal oxide such as V₂O₅ is added to make a catalyst, the DeNO_x activity is greater than a similar catalyst made without the barium sulfate addition. The preferred amount of barium sulfate to be added is from 1 to 15 wt% of the formed metal oxide support.

A preferable inexpensive inorganic oxide support is silica (either gel or precipitated) such as Syloid 74 (W. R. Grace & Co.) or Zeofinn XP-113 (Zeofinn Oy, Finland). Preferably, the surface area of the support

with the titania and catalyst is from a catalytically effective amount up to $350 \text{ m}^2/\text{cm}^3$, or, more preferably, one that is between $25 \text{ m}^2/\text{cm}^3$ and $200 \text{ m}^2/\text{cm}^3$. Preferably the pore diameter distribution of the formed body should cover the range from 0 - 10 000 nm (0 to 100,000 Angstrom units). Preferably the support should have a micropore diameter distribution between 0 and 60 nm (0 and 600 Angstrom units), more preferably between 5 and 15 nm (50 and 150 Angstrom units), and a macropore diameter distribution between 60 and 10 000 nm (600 and 100,000 Angstrom units), more preferably between 100 and 2000 nm (1,000 and 20,000 Angstrom units). Although the mathematical model tends to maximize the porosity, we prefer, due to the limitation of strength, a maximum total porosity of $0.80 \text{ cm}^3/\text{cm}^3$, or more preferably, between 0.5 and $0.75 \text{ cm}^3/\text{cm}^3$. The microporosity is preferably between 0.05 and $0.50 \text{ cm}^3/\text{cm}^3$ and macroporosity preferably between 0.05 and $0.50 \text{ cm}^3/\text{cm}^3$.

Description of the Preferred Embodiments

When making the catalyst support with titania particles alone, it is preferable to mix burnout materials with the titania particles and to then form the mixture into the desired shape such as a monolith. Examples of burnout materials are polyethylene oxide, methylcellulose, starch or flour, polyethylene or any of the polymeric microspheres or microwaxes. To aid in extrusion conventional binders and extrusion aids can be added such as clay, glass fibers, and polyethylene oxide. Optionally porous inorganic oxide particles can be added in an amount up to 40% by weight to the titania particles to give the resultant mixture the desired macroporosity. Again, burnout materials can also be added to provide additional macroporosity and extrusion aids can also be added. The formed catalyst support has a total porosity of up to $0.80 \text{ cm}^3/\text{cm}^3$ of the formed catalyst which is made up of a micropore porosity (comprising pores having a pore diameter 60 nm (600 Angstrom units) or less) of 0.05 to $0.5 \text{ cm}^3/\text{cm}^3$ and a macroporosity (comprising pores having diameters greater than 60 nm (600 Angstrom units)) of 0.05 to $0.5 \text{ cm}^3/\text{cm}^3$. The titania is present substantially in the anatase phase. The catalyst is made by depositing on the support a metal oxide catalytic component such as V_2O_5 , MoO_3 , WO_3 , Fe_2O_3 , CuSO_4 , VOSO_4 , Mn_2O_3 , Mn_3O_4 , or mixtures thereof. Preferably the metal oxide is present in an amount from a catalytically effective amount to 25% by weight of the entire catalyst.

The support is calcined for about 2 hours preferably between 300 - 900°C more preferably 400 - 650°C . The final fraction of titania of the total support is between 5 and 80 wt%, preferably between 15 and 50 wt%. Below 5 wt% the catalyst has a low activity and above about 80 wt% the catalyst becomes economically unattractive to manufacture.

The formed support is characterized by porosity which is measured in units of cm^3/cm^3 . The porosity is obtained from the pore volume of the support and the bulk density. For example, for a support having a pore volume of $0.96 \text{ cm}^3/\text{g}$ and a bulk density of $0.75 \text{ g}/\text{cm}^3$, the porosity would be the product of these two values which is $0.72 \text{ cm}^3/\text{cm}^3$.

The catalyst is made by adding to the calcined support metal oxides such as V_2O_5 , MoO_3 , WO_3 , Fe_2O_3 , CuSO_4 , VOSO_4 , SnO_2 , Mn_2O_3 , Mn_3O_4 or a combination thereof. The catalyst component or components are added to the support either before or after the support shape is formed. The amount of the catalyst component is from a catalytically effective amount up to 25% by weight of the entire catalyst.

The catalyst may be prepared by one of several means. Thus, for example, the TiO_2 -inorganic oxide support can first be impregnated with WO_3 before or after extrusion. For this purpose, an aqueous solution of ammonium metatungstate may be used to impregnate the support to incipient wetness. The amount of ammonium metatungstate to be used depends on the desired final percentage of WO_3 (which may preferably range from 1 to 20 wt%). The impregnated support may then be dried and calcined for example at 500 - 550°C . for 2 hours.

The support, with or without WO_3 , can then be impregnated with V_2O_5 before or after the extruded body is formed. The V_2O_5 precursor used can be an aqueous solution of vanadyl oxalate at a concentration which is appropriate to give the final desired V_2O_5 content (typically 0.5-20 wt%) in the catalyst. If the impregnation is to be carried out before the extrusion, then the support powder may be impregnated to incipient wetness with the V_2O_5 precursor solution followed by drying (100 - 150°C . for about 12 hours). The dried powder can then be used for extrusion. Alternatively, if the V_2O_5 is to be impregnated after the extrusion, the extruded body is first dried and calcined (for example, at 500 - 550°C . for 2 hours) and then dipped in the appropriate V_2O_5 precursor solution. The extrusion can be carried out in a number of ways familiar to those skillful in the art.

The present catalyst is characterized by the presence of titania in the anatase phase. When silica is used as the metal oxide, the titania/silica product is not a chemical composite on the atomic scale. Instead, it is a physical mixture with anatase titania. The anatase titania particle size, as measured by the X-ray line

broadening method (H.P. Klug and L.E. Alexander, "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials") typically averages about 5 nm (50 Angstrom units). It can also be measured by EXAFS (extended X-ray absorption fine structure).

It is important to point out here that for the purpose of this invention, it is undesirable, indeed disadvantageous, to have a silica-titania chemical composite such as described in U. S. Patent 4,221,768 and GB 2,149,680. The latter patents teach the preparation of a Ti-Si composite oxide wherein the final product does not contain a distinct anatase titania phase. Similarly U. S. Patent 4,176,089 also has a co-precipitation which results in an undesirable catalyst because the anatase phase would not be present. In the present case, our final titania/silica product shows the presence of titania anatase phase and it is not a chemical composite on the atomic scale. It is of finely dispersed anatase titania and silica.

The inorganic oxide chosen should largely determine the desired pore structure in the formed catalyst. The desired pore structure should have an average micropore diameter of less than 60 nm (600 Angstrom units), more preferably between 5 and 15 nm (50 and 150 Angstrom units) and a macropore diameter distribution between 60 and 10 000 nm (600 and 100,000 Angstrom units), more preferably between 100 and 2000 nm (1000 and 20,000 Angstrom units). If the inorganic oxide does not give the desired pore structure, burn-out material may be added to give the right amount of macroporosity. In the latter case, one of several burn-out materials may be used including, but not limited to, polyethylene oxide, methylcellulose, starch or flour, polyethylene or any of the polymeric microspheres or microwaxes.

In another preferred embodiment, BaSO_4 is added. This appears to add sulfate in the support which is advantageous for higher activity. The barium sulfate can be added as barium sulfate or as a soluble barium salt precursor such as barium chloride, barium nitrate, barium acetate, barium hydroxide or mixtures of these salts. Conversion to barium sulfate is achieved by adding sulfuric acid.

Having described the basic aspects of our invention, the following examples are given to illustrate specific embodiments thereof.

Example 1

A comparison catalyst was prepared from anatase TiO_2 .

A solution of vanadyl oxalate was prepared by dissolving 0.097 g of NH_4VO_3 and 0.194 g of oxalic acid into 10 ml of hot water. The solution was used to impregnate 15.0 g of TiO_2 powder having a surface area of 100 m^2/g using the method of incipient wetness. The resulting dried powder was calcined at 520 °C for 3 hours.

Example 2

This comparison example prepares a catalyst from a physical mixture of anatase TiO_2 and silica.

A solution of vanadyl oxalate was prepared by dissolving 0.097 g of NH_4VO_3 and 0.194 g of oxalic acid in 28 ml of hot water. The solution was used to impregnate a mixture of 6 g of TiO_2 powder (Sakai Chemical) and 9 g of SiO_2 powder (Davison 952 W. R. Grace & Co.) using the method of incipient wetness. The powder was calcined at 520 °C for 3 hours.

Example 3

This comparison example prepares a catalyst where the silica and titania form a binary oxide as described in U. S. Patent No. 4,221,768.

A support was prepared following the procedure of Example 1 of U.S. Patent No. 4,221,768 as follows. 50 ml of titanyl chloride solution (Kemira Unitil 102, containing 342 g TiO_2 per liter) was diluted to 200 ml with ice cold water. Then, 76.5 g of Nalco 1034A colloidal silica (34% SiO_2) was added. While the mixture was stirred at about 25 °C, aqueous ammonia was slowly added until the pH reached 9.7. The mixture was aged by allowing it to stand for 2 hours. The resulting TiO_2 - SiO_2 gel was isolated by filtration, washed with water, and dried at 150 °C for 10 hours. The solid was ground and calcined at 500 °C for 3 hours. The resulting powder was found by BET analysis to have a surface area of 253 m^2/cm^3 . Analysis by X-ray diffraction demonstrated that the product was amorphous.

A solution of vanadyl oxalate was prepared by dissolving 0.56 g of V_2O_5 and 1.44 g of oxalic acid in 15 ml of hot H_2O . The solution was used to impregnate 15.0 g of the above TiO_2 - SiO_2 powder using the method of incipient wetness. The powder was calcined at 520 °C for 3 hours.

Example 4

The activities of the catalyst powders of Examples 1-3 were determined as follows.

In a fixed bed reactor, 0.58 cm³ of powder were charged and the fixed bed reactor was heated in a sand bath to the temperatures set forth in Table 1. A gas containing 900 ppm NO, 1000 ppm NH₃, and 4% O₂ in N₂ was passed through the catalyst bed at a rate of 200 l/h. and the amount of NO removed measured. The results are presented in Table 1.

TABLE 1

Example	Activity of Catalyst Powders		
	% Conversion		
	250 °C	300 °C	350 °C
1	10.5	33.8	74.3
2	7.4	22.2	42.7
3	16.7	33.8	57.2

The catalyst of Example 1, prepared from anatase TiO₂, is representative of the composition of current commercial SCR catalyst and is shown to have poorer performance than the catalysts of this invention. Physical mixture of silica with such an anatase TiO₂ support leads to a lowered NOx conversion as shown by the catalyst of Example 2. An atomically mixed support, demonstrated by Example 3, also is shown to have poorer performance.

Example 5

This example shows a commercial catalyst.

The activity of a monolithic shaped commercial catalyst which was based on TiO₂ with near zero macroporosity was obtained. Reactor conditions used were: 6% O₂, 10% H₂O, 350 °C; 400 ppm NO; 3000 ppm SO₂; 400 ppm NH₃; SV 7500 h⁻¹ (STP).

The Table 2 below shows the porosity and NOx removal activity ratio of the commercial catalyst.

TABLE 2

Catalyst	Porosity (cm ³ /cm ³)		Activity Ratio (1)
	Microporosity Less than (600 AU) 60 nm	Macroporosity greater than (600 AU) 60 nm	
Commercial catalyst	0.49	0.03	1.0
Where AU is Angstrom units			

(1) Data obtained after 9 days continuous running. The activity ratio is that of reaction rate constants with that of the commercial catalyst set at 1.0.

Example 6

This example described the preparation of a catalyst powder for extrusion.

A titania catalyst powder suitable for extrusion was prepared as follows. 1690 g of titania powder was combined with 48 g of clay and the mixture dried at 200 °C. A solution of 7.57 g of vanadium and 30.30 g of oxalic acid in 280 ml of water was prepared and combined with a solution of 150.9 g of ammonium tungstate in 300 ml of water. The solution was then used to impregnate the mixture of titania and clay. The product was dried at 110 °C, ground, and sieved to below 0.177 mm sieve opening (80 mesh).

Example 7

This is a comparison example which describes the extrusion of bodies without the introduction of macroporosity.

A mixture of 100 g of the powder prepared in Example 6 was made with 2.5 g of Methocel 20-213 (Dow Chemical Co.) and 35 ml of water. The mixture was extruded to produce 0.32 cm (1/8") diameter cylinders which were dried and calcined at 550°C. The resultant cylinders were analyzed by mercury intrusion porosimetry and found to contain only a small fraction of macroporosity (0.05 cm³ of pores with diameters greater than 60 nm (600 Angstrom units)/cm³ of total volume).

Example 8

This example describes the extrusion of bodies containing macropores.

A mixture of 100 g of the powder prepared in Example 6 was made with 15 g of Methocel 20-213 (Dow Chemical Co.) and 45 ml of water. The mixture was extruded to produce 0.32 cm (1/8") diameter cylinders which were dried and calcined at 550°C. The resultant cylinders were analyzed by mercury intrusion porosimetry and found to contain a substantial fraction of macroporosity (0.17 cm³ of pores with diameters greater than 60 nm (600 Angstrom units)/cm³ of total volume).

Example 9

This example describes the extrusion of bodies containing macropores and which further contain silica.

A mixture of 100 g of the powder prepared in Example 10 was made with 20 g of Methocel 20-213 (Dow Chemical Co.), 11.1 g of silica (Syloid 63, Davison Chemical), and 35 ml of water. The mixture was extruded to produce 0.32 cm (1/8") diameter cylinders which were dried and calcined at 550°C. The resultant cylinders were analyzed by mercury intrusion porosimetry and found to contain a substantial fraction of macroporosity (0.21 cm³ of pores with diameters greater than 60 nm (600 Angstrom units)/cm³ of total volume).

Example 10

This example measures the activity of the extrudates of Examples 7-9.

The activities of the extrudates described Examples 7, 8 and 9 were determined as follows. In a fixed bed reactor, about 0.3 cm³ of extrudates were charged and the fixed bed reactor was heated in a sand bath to the temperatures set forth in Table 3 below. A gas containing 1275 ppm of NO, 1275 ppm of NH₃, and 4% O₂ in N₂ was passed through the catalyst bed at a rate of 200 l/h and the amount of NO removed was measured. The rate of NO removal was calculated and the results are presented in Table 3.

TABLE 3

Rate of NO Removal by 0.32 cm (1/8 inch) extrudates				
Example	Porosity (a)		10 ⁷ mole NO removed/cm ² -sec	
	Total	Macropores	310°C	380°C
7	0.54	0.05	6.9	11.0
8	0.60	0.17	9.2	15.4
9	0.58	0.21	8.5	14.9

(a) Porosity is defined as cm³ of pore volume/cm³ of total volume. Total includes all pores and macropores are those pores with diameters greater than 60 nm (600 Angstrom Units).

The data in Table 3 demonstrate the improved performance obtained by the introduction of macroporosity. The catalyst prepared in Example 8 differs from that in Example 7 only in the presence of the additional macroporosity and it is substantially more active than the catalyst of Example 7. The catalyst of Example 9 demonstrates that the presence of such macroporosity allows further addition to the catalyst by an inexpensive porous material such as silica while maintaining a high activity.

Claims

1. A catalyst for the selective removal of nitrogen oxides from exhaust and waste gases in the presence of ammonia comprising:
 - (a) a formed porous support made either of titania particles alone or of a mixture of titania particles with particles of another porous inorganic oxide, said formed support having
 - (i) a total porosity of up to $0.80 \text{ cm}^3/\text{cm}^3$ which is made up of a micropore porosity, comprising pores having a pore diameter of 60 nm (600 \AA) or less, of 0.05 to $0.5 \text{ cm}^3/\text{cm}^3$ and a macroporosity, comprising pores having diameters greater than 60 nm (600 \AA), of 0.05 to $0.5 \text{ cm}^3/\text{cm}^3$, and
 - (ii) said titania being substantially present in the anatase phase, and
 - (b) a metal oxide catalytic component deposited on said support selected from the group consisting of V_2O_5 , MoO_3 , WO_3 , Fe_2O_3 , CuSO_4 , VOSO_4 , SnO_2 , Mn_2O_3 , Mn_3O_4 , and mixtures thereof, said metal oxide being present in an amount from a catalytically effective amount to 25% by weight of the entire catalyst.
2. A catalyst according to Claim 1, wherein said inorganic oxide is selected from the group consisting of SiO_2 , Al_2O_3 , ZrO_2 , AlPO_4 , Fe_2O_3 , B_2O_3 and mixtures thereof.
3. A catalyst according to Claims 1 or 2, wherein the surface area of the catalyst is less than $350 \text{ m}^2/\text{cm}^3$.
4. A catalyst according to any of Claims 1 to 3, wherein the surface area of the catalyst is between 25 and $200 \text{ m}^2/\text{cm}^3$.
5. A catalyst according to any of Claims 1 to 4, further comprising barium sulfate in an amount of from 1 to 15% by weight of the formed support.
6. A catalyst according to any of Claims 1 to 5, wherein said porous inorganic oxide is silica gel or precipitated silica.
7. A catalyst according to any of Claims 1 to 6, wherein the catalyst is shaped as a monolith, extrudate, bead, or plate.
8. A catalyst according to any of Claims 1 to 7, wherein the catalyst is shaped as a monolith.
9. A catalyst according to any of Claims 1 to 8, wherein said inorganic oxide is present in an amount up to 40% by weight.
10. A catalyst according to any of Claims 1 to 8, wherein the support comprises titania and at least one other inorganic oxide and contains titania in an amount of 5 to $80 \text{ wt}\%$.
11. A catalyst according to any of Claims 1 to 10, wherein the total porosity is between 0.5 and $0.8 \text{ cm}^3/\text{cm}^3$.
12. A catalyst according to Claims 10 or 11, wherein the titania is present in an amount of between about 15 to $50 \text{ wt}\%$ of the total support.
13. A catalyst according to any of Claims 10 to 12, wherein the pore size distribution of the formed body is in pores having a pore diameter in the range of greater than 0 to $10 \text{ }\mu\text{m}$ (0 to $100,000 \text{ \AA}$).
14. A catalyst according to any of claims 10 to 13, wherein the formed body has a micropore size distribution, comprising pores having a pore diameter of 60 nm (600 \AA) or less, having an average pore diameter of $5 - 15 \text{ nm}$ ($50 - 150 \text{ \AA}$) and a macropore size distribution, comprising pores with a pore diameter between greater than 60 nm and $10 \text{ }\mu\text{m}$ (600 and $100,000 \text{ \AA}$), having an average pore diameter between 100 nm and $2 \text{ }\mu\text{m}$ (1000 and $20,000 \text{ \AA}$).
15. A catalyst according to any of Claims 10 to 14, wherein the average micropore diameter is between $8 - 12 \text{ nm}$ (80 and 120 \AA) and wherein the average micropore diameter is between 500 nm and $1.5 \text{ }\mu\text{m}$

(5000 and 15000 Å).

16. A process for making a DeNO_x catalyst comprising the steps of
 - (a) forming a porous shaped support either from titania particles or from a mixture of titania particles with particles of another porous inorganic oxid, said support having
 - (i) a total porosity of up to 0.80 cm³/cm³ which is made up of a micropore porosity, comprising pores having a pore diameter of 0 - 60 nm (0 - 600 Å), of 0.05 to 0.5 cm³/cm³ and a macroporosity (comprising pores having diameters greater than 50nm (600 Å) of 0.05 to 0.5 cm³/cm³, and
 - (ii) said titania being substantially present in the anatase phase; and
 - (b) depositing a metal oxide catalytic component on said support selected from the group consisting of V₂O₅, MoO₃, WO₃, Fe₂O₃, CuSO₄, VOSO₄, Mn₂O₃, SnO₂, Mn₂O₄, and mixtures thereof, said metal oxide being present in an amount from a catalytically effective amount to 25% by weight of the entire catalyst.
17. A process according to Claim 16, wherein said inorganic oxide is selected from the group consisting of SiO₂, Al₂O₃, ZrO₂, AlPO₄, Fe₂O₃, B₂O₃ and mixtures thereof.
18. A process according to claims 16 or 17, wherein the catalyst is shaped as a monolith, extrudate, bead, or plate.
19. A process according to any of Claims 16 to 18, wherein the catalyst further comprises barium sulfate in an amount of from 1 - 15% by weight of the formed support.
20. A process according to any of Claims 16 to 19, wherein said porous inorganic oxide is silica gel or precipitated silica.
21. A process according to any of Claims 16 to 20, wherein said inorganic oxide is present in an amount up to 40% by weight.
22. A process according to any of Claims 16 to 21, comprising forming the support into an extruded monolith.
23. A process according to Claim 22, wherein said BaSO₄ or a soluble barium salt precursor which will form BaSO₄ upon reacting is added to said inorganic oxide.
24. A process according to Claim 22, wherein said BaSO₄ is added with or before the titania.
25. A process according to Claim 23, wherein the barium sulfate precursor is selected from the group consisting of barium chloride, barium nitrite, barium acetate, barium hydroxide and mixtures thereof.
26. A process for the selective removal of nitrogen oxides from exhaust and waste gases, which comprises contacting the exhaust or waste gases with ammonia at a temperature of from about 150 °C to about 500 °C in the presence of a catalyst as described in Claims 1 to 15.

Patentansprüche

1. Katalysator für die selektive Entfernung von Stickstoffoxiden aus Auspuff- und Abgasen in Gegenwart von Ammoniak, der
 - (a) einen geformten porösen Träger aus entweder Titandioxidteilchen allein oder aus einer Mischung von Titandioxidteilchen mit Teilchen von anderem, porösem, anorganischem Oxid, wobei der geformte Träger
 - (i) eine Gesamtporosität von bis zu 0,80 cm³/cm³ aufweist, die aus einer Mikroporenporosität, die Poren mit einem Porendurchmesser von 60 nm (600 Å) oder weniger umfaßt, von 0,05 bis 0,5 cm³/cm³ und einer Makroporosität, die Poren mit Durchmessern größer als 60 nm (600 Å) umfaßt, von 0,05 bis 0,5 cm³/cm³ gebildet ist, und
 - (ii) das Titandioxid im wesentlichen in der Anatasephase vorliegt, und

(b) eine katalytische Metalloxydkomponente aufgebracht auf den Träger und ausgewählt aus der Gruppe bestehend aus V_2O_5 , MoO_3 , WO_3 , Fe_2O_3 , $CuSO_4$, $VOSO_4$, SnO_2 , Mn_2O_3 , Mn_2O_4 und Mischungen derselben umfaßt, wobei das Metalloxyd in einer Menge von einer katalytisch wirksamen Menge bis zu 25 Gew.-% des gesamten Katalysators vorliegt.

2. Katalysator nach Anspruch 1, bei dem das anorganische Oxid ausgewählt ist aus der Gruppe bestehend aus SiO_2 , Al_2O_3 , ZrO_2 , $AlPO_4$, Fe_2O_3 , B_2O_3 und Mischungen derselben.
3. Katalysator nach den Ansprüchen 1 oder 2, bei dem die Oberfläche des Katalysators kleiner als $350 \text{ m}^2/\text{cm}^3$ ist.
4. Katalysator nach einem der Ansprüche 1 bis 3, bei dem die Oberfläche des Katalysators zwischen 25 und $200 \text{ m}^2/\text{cm}^3$ liegt.
5. Katalysator nach einem der Ansprüche 1 bis 4, der ferner Bariumsulfat in einer Menge von 1 bis 15 Gew.-% des geformten Trägers umfaßt.
6. Katalysator nach einem der Ansprüche 1 bis 5, bei dem das poröse anorganische Oxid Siliciumdioxid-gel oder ausgefälltes Siliciumdioxid ist.
7. Katalysator nach einem der Ansprüche 1 bis 6, bei dem der Katalysator als Monolith, Extrudat, Kugel oder Platte ausgestaltet ist.
8. Katalysator nach einem der Ansprüche 1 bis 7, bei dem der Katalysator als Monolith ausgestaltet ist.
9. Katalysator nach einem der Ansprüche 1 bis 8, bei dem das anorganische Oxid in einer Menge von bis zu 40 Gew.-% vorhanden ist.
10. Katalysator nach einem der Ansprüche 1 bis 8, bei dem der Träger Titandioxid und mindestens ein anderes anorganisches Oxid umfaßt und Titandioxid in einer Menge von 5 bis 80 Gew.-% enthält.
11. Katalysator nach einem der Ansprüche 1 bis 10, bei dem die Gesamtporosität zwischen 0,5 und $0,8 \text{ cm}^3/\text{cm}^3$ liegt.
12. Katalysator nach Anspruch 10 oder 11, bei dem das Titandioxid in einer Menge zwischen etwa 15 bis 50 Gew.-% des gesamten Trägers vorhanden ist.
13. Katalysator nach einem der Ansprüche 10 bis 12, bei dem die Porengrößenverteilung des geformten Körpers in Poren mit einem Porendurchmesser im Bereich von größer als 0 bis $10 \text{ }\mu\text{m}$ (0 bis $100\,000 \text{ }\text{\AA}$) vorliegt.
14. Katalysator nach einem der Ansprüche 10 bis 13, bei dem der geformte Körper eine Mikroporengrößenverteilung aufweist, die Poren mit einem Porendurchmesser von 60 nm ($600 \text{ }\text{\AA}$) oder weniger mit einer durchschnittlichen Porendurchmesser von 5 bis 15 nm (50 bis $150 \text{ }\text{\AA}$) umfaßt, und eine Makroporengrößenverteilung aufweist, die Poren mit einem Porendurchmesser zwischen größer als 60 nm und $10 \text{ }\mu\text{m}$ (600 und $100\,000 \text{ }\text{\AA}$) mit einem durchschnittlichen Porendurchmesser zwischen 100 nm und $2 \text{ }\mu\text{m}$ (1000 und $20\,000 \text{ }\text{\AA}$) umfaßt.
15. Katalysator nach einem der Ansprüche 10 bis 14, bei dem der durchschnittliche Mikroporendurchmesser zwischen 8 und 12 nm (80 und $120 \text{ }\text{\AA}$) liegt und der durchschnittliche Makroporendurchmesser zwischen 500 nm und $1,5 \text{ }\mu\text{m}$ (5000 und $15\,000 \text{ }\text{\AA}$) liegt.
16. Verfahren zur Herstellung eines DeNOx-Katalysators, bei dem
 - (a) ein poröser geformter Träger entweder aus Titandioxidteilchen oder aus einer Mischung von Titandioxidteilchen mit Teilchen von anderem, porösem, anorganischem Oxid gebildet wird, wobei der Träger
 - (i) eine Gesamtporosität von bis zu $0,80 \text{ cm}^3/\text{cm}^3$ aufweist, die aus einer Mikroporenporosität, die Poren mit einem Porendurchmesser von 0 bis 60 nm (0 bis $600 \text{ }\text{\AA}$) umfaßt, von 0,05 bis 0,5

- cm³/cm³, und einer Makroporosität, die Poren mit Durchmessern größer als 60 nm (600 Å) umfaßt, von 0,05 bis 0,5 cm³/cm³ gebildet ist, und
- (ii) das Titandioxid im wesentlichen in Anatasephase vorliegt, und
- (b) eine katalytische Metalloxydskomponente auf dem Träger aufgebracht wird, die ausgewählt ist aus der Gruppe bestehend aus V₂O₅, MoO₃, WO₃, Fe₂O₃, CuSO₄, VOSO₄, Mn₂O₃, SnO₂, Mn₂O₄ und Mischungen derselben, wobei das Metalloxyd in einer Menge von einer katalytisch wirksamen Menge bis zu 25 Gew.-% des gesamten Katalysators vorliegt.
17. Verfahren nach Anspruch 16, bei dem das anorganische Oxid ausgewählt ist aus der Gruppe bestehend aus SiO₂, Al₂O₃, ZrO₂, AlPO₄, Fe₂O₃, B₂O₃ und Mischungen derselben.
18. Verfahren nach Anspruch 16 oder 17, bei dem der Katalysator als Monolith, Extrudat, Kugel oder Platte ausgestaltet ist.
19. Verfahren nach einem der Ansprüche 16 bis 18, bei dem der Katalysator ferner Bariumsulfat in einer Menge von 1 bis 15 Gew.-% des geformten Trägers umfaßt.
20. Verfahren nach einem der Ansprüche 16 bis 19, bei dem das poröse anorganische Oxid Siliciumdioxid-gel oder ausgefälltes Siliciumdioxid ist.
21. Verfahren nach einem der Ansprüche 16 bis 20, bei dem das anorganische Oxid in einer Menge von bis zu 40 Gew.-% vorhanden ist.
22. Verfahren nach einem der Ansprüche 16 bis 21, bei dem der Träger zu einem extrudierten Monolith geformt wird.
23. Verfahren nach Anspruch 22, bei dem das BaSO₄ oder ein löslicher Bariumsalzvorläufer, der BaSO₄ bei der Umsetzung bildet, zu dem anorganischen Oxid gegeben wird.
24. Verfahren nach Anspruch 22, bei dem das BaSO₄ zusammen mit oder vor dem Titandioxid zugesetzt wird.
25. Verfahren nach Anspruch 23, bei dem der Bariumsulfatvorläufer ausgewählt ist aus der Gruppe bestehend aus Bariumchlorid, Bariumnitrit, Bariumhydroxid und Mischungen derselben.
26. Verfahren zur selektiven Entfernung von Stickstoffoxiden aus Auspuff- und Abgasen, bei dem das Auspuff- oder Abgas mit Ammoniak bei einer Temperatur von etwa 150 °C bis etwa 500 °C in Gegenwart eines Katalysators wie beschrieben in den Ansprüchen 1 bis 15 in Kontakt gebracht wird.
- Revendications**
1. Catalyseur pour l'élimination sélective des oxydes d'azote à partir de gaz d'échappement et résiduels en présence d'ammoniac, comprenant :
- a) un support poreux formé, composé de particules d'oxyde de titane ou d'un mélange de particules d'oxyde de titane et de particules d'un autre oxyde inorganique poreux, le support formé ayant :
- (i) une porosité totale de jusqu'à 0,80 cm³ par cm³, qui est constituée d'une microporosité comprenant des pores ayant un diamètre des pores de 60 nm (600 Å) ou moins, de 0,05 à 0,5 cm³ par cm³ et une macroporosité, comprenant des pores ayant un diamètre supérieur à 60 nm (600 Å), de 0,05 à 0,5 cm³ par cm³, et
- (ii) l'oxyde de titane étant sensiblement présent sous la phase anatase, et
- b) un composant catalytique d'un oxyde métallique, déposé sur le support, choisi parmi le groupe consistant en V₂O₅, MoO₃, WO₃, Fe₂O₃, CuSO₄, VOSO₄, SnO₂, Mn₂O₃, Mn₂O₄ et les mélanges de ceux-ci, l'oxyde métallique étant présent en une quantité allant d'une quantité catalytiquement efficace à 25% en poids du catalyseur entier.
2. Catalyseur suivant la revendication 1, dans lequel l'oxyde inorganique est choisi parmi le groupe consistant en SiO₂, Al₂O₃, ZrO₂, AlPO₄, Fe₂O₃, B₂O₃ et leurs mélanges.

3. Catalyseur suivant la revendication 1 ou 2, dans lequel la surface spécifique du catalyseur est inférieure à 350 m² par cm³.
- 5 4. Catalyseur suivant l'une quelconque des revendications 1 à 3, dans lequel la surface spécifique du catalyseur se situe entre 25 et 200 m² par cm³.
5. Catalyseur suivant l'une quelconque des revendications 1 à 4, comprenant, en outre, du sulfate de baryum en une quantité de 1 à 15% en poids du support formé.
- 10 6. Catalyseur suivant l'une quelconque des revendications 1 à 5, dans lequel l'oxyde inorganique poreux est du gel de silice ou de la silice précipitée.
7. Catalyseur suivant l'une quelconque des revendications 1 à 6, dans lequel le catalyseur a la forme d'un monolithe, d'un profilé, d'un cordon ou d'une plaque.
- 15 8. Catalyseur suivant l'une quelconque des revendications 1 à 7, dans lequel le catalyseur a la forme d'un monolithe.
9. Catalyseur suivant l'une quelconque des revendications 1 à 8, dans lequel l'oxyde inorganique est présent en une quantité pouvant aller jusqu'à 40% en poids.
- 20 10. Catalyseur suivant l'une quelconque des revendications 1 à 8, dans lequel le support comprend de l'oxyde de titane et au moins un autre oxyde inorganique et contient l'oxyde de titane en une quantité de 5 à 80% en poids.
- 25 11. Catalyseur suivant l'une quelconque des revendications 1 à 10, dans lequel la porosité totale se situe entre 0,5 et 0,8 cm³ par cm³.
- 30 12. Catalyseur suivant la revendication 10 ou 11, dans lequel l'oxyde de titane est présent en une quantité d'environ 15 à 50% en poids du support total.
13. Catalyseur suivant l'une quelconque des revendications 10 à 12, dans lequel la distribution de la taille des pores dans le corps formé est constituée de pores ayant un diamètre des pores dans l'intervalle de plus de 0 à 10 µm (0 à 100 000 Å).
- 35 14. Catalyseur suivant l'une quelconque des revendications 10 à 13, dans lequel le corps formé a une distribution de la taille des micropores, comprenant les pores ayant un diamètre des pores de 60 nm (600 Å) ou moins, et ayant un diamètre moyen des pores de 5 à 15 nm (50 à 150 Å) et une distribution de la taille des macropores, comprenant les pores ayant un diamètre des pores se situant entre plus de 60 nm et 10 µm (600 et 100 000 Å), ayant un diamètre moyen des pores entre 100 nm et 2 µm (1000 et 20 000 Å).
- 40 15. Catalyseur suivant l'une quelconque des revendications 10 à 14, dans lequel le diamètre moyen des pores se situe entre 8 et 12 nm (80 et 120 Å) et dans lequel le diamètre moyen des macropores se situe entre 500 nm et 1,5 µm (5000 et 15 000 Å).
- 45 16. Procédé de préparation d'un catalyseur de dénitruration, comprenant les étapes de :
 - (a) formation d'un support poreux façonné, composé de particules d'oxyde de titane ou d'un mélange de particules d'oxyde de titane et de particules d'un autre oxyde inorganique poreux, le support ayant :
 - (i) une porosité totale de jusqu'à 0,80 cm³ par cm³, qui est constituée d'une microporosité comprenant des pores ayant un diamètre des pores de 0 à 60 nm (0 à 600 Å), de 0,05 à 0,5 cm³ par cm³ et d'une macroporosité, comprenant des pores ayant un diamètre supérieur à 60 nm (600 Å), de 0,05 à 0,5 cm³ par cm³, et
 - 50 (ii) l'oxyde de titane étant sensiblement présent sous la phase anatase, et
 - b) dépôt d'un composant catalytique d'un oxyde métallique sur le support, choisi parmi le groupe consistant en V₂O₅, MnO₂, WO₃, Fe₂O₃, CuSO₄, VOSO₄, Mn₂O₃, SnO₂, Mn₂O₄ et les mélanges de ceux-ci, l'oxyde métallique étant présent en une quantité allant d'une quantité catalytiquement

efficace à 25% en poids du catalyseur entier.

17. Procédé suivant la revendication 16, dans lequel l'oxyde inorganique est choisi parmi le groupe consistant en SiO_2 , Al_2O_3 , ZrO_2 , AlPO_4 , Fe_2O_3 , B_2O_3 et leurs mélanges.
18. Procédé suivant la revendication 16 ou 17, dans lequel le catalyseur est façonné comme un monolithe, un profilé, un cordon ou une plaque.
19. Procédé suivant l'une quelconque des revendications 16 à 18, dans lequel le catalyseur comprend, en outre, du sulfate de baryum en une quantité de 1 à 15% en poids du support formé.
20. Procédé suivant l'une quelconque des revendications 16 à 19, dans lequel l'oxyde inorganique poreux est du gel de silice ou de la silice précipitée.
21. Procédé suivant l'une quelconque des revendications 16 à 20, dans lequel l'oxyde inorganique est présent en une quantité pouvant aller jusqu'à 40% en poids.
22. Procédé suivant l'une quelconque des revendications 16 à 21, comprenant la formation du support en un monolithe extrudé.
23. Procédé suivant la revendication 22, dans lequel le BaSO_4 ou un précurseur sel de baryum soluble, qui peut former du BaSO_4 par réaction, est ajouté à l'oxyde inorganique.
24. Procédé suivant la revendication 22, dans lequel le BaSO_4 est ajouté avec ou avant l'oxyde de titane.
25. Procédé suivant la revendication 23, dans lequel le précurseur du sulfate de baryum est choisi parmi le groupe consistant en chlorure de baryum, nitrite de baryum, acétate de baryum, hydroxyde de baryum et leurs mélanges.
26. Procédé pour l'élimination sélective des oxydes d'azote de gaz d'échappement ou résiduels, qui comprend la mise en contact des gaz d'échappement ou résiduels avec de l'ammoniac, à une température d'environ 150°C à environ 500°C , en présence d'un catalyseur tel que décrit dans les revendications 1 à 15.

